Sorption of Uranium (VI) to Graphite under Potential Repository Conditions

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Outline

- Graphite in Geological Repository Systems
- Experimental Methodology
- Graphite Characterization
- Results
  - Effect of pH on Equilibrium Sorption
  - Carbonate and Ionic Strength
  - Sorption Kinetics and Desorption
  - Sorption Isotherms
- Conclusions & Future Work
HTGR Fuel Disposal

BWR Fuel\(^1\)

TRISO Fuel\(^2\)

Pyrolytic Carbon
Silicon Carbide
Porous Carbon Buffer
Oxide Fuel (TRUO\(_{1.68}\))

\{ TRISO Coating \}
Backfill Applications

Drift Backfill

Borehole Casing/Backfill

http://www.tms.org/pubs/journals/JOM/0009/Yim-0009.html
Experimental Methodology

- Stock Solutions
  - Depleted uranium – $\text{UO}_2(\text{NO}_3)_2$ in 0.01 M HCl
  - Spiked with $^{233}\text{U}$ (Eckert & Ziegler) - 100 Bq/sample

- Analysis by Liquid Scintillation Counting

- Batch Experiments – Common Parameters
  - 10 mL:1g solution to graphite ratio
  - 10 samples per data point (7 samples, 3 blanks)
  - $I = 0.01\text{M NaCl}$
  - pH controlled by addition of 0.01 M HCl or NaOH
    - Borax buffer used for pH 7 to 10 region
  - FEP Tubes used from pH 6 to 8 to minimize sorption
  - Mixed on Hematology Mixer for 5 days, Centrifuge to Separate
Graphite Characterization

- Alpha Aesar (-20/+100)
- X-Ray Diffraction
  - No minor phases observed
- FTIR Spectroscopy
  - 1631 suggests sp²-hybridized C
  - 1384 suggests C-OH formation
  - 3477 suggests surface water or hydrogen-bonded OH groups
- BET Surface Area
  - 0.554 ± 0.027 m²/g
- Proton Exchange Capacity
  - 0.25 ± 0.15 cmol/kg
- Point of Zero Charge
  - pH = 9.3
Equilibrium Sorption – pH Effects

(K_d = 126 ± 7.0 ml/g)
Equilibrium Sorption vs. Speciation

Speciation Curve Generated using EQ3/6 with the YM Database
Effect of Ionic Strength

<table>
<thead>
<tr>
<th>pH</th>
<th>[NaCl] (molal)</th>
<th>K&lt;sub&gt;d&lt;/sub&gt; (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.03</td>
<td>0.01</td>
<td>8.23 ± 0.08</td>
</tr>
<tr>
<td>4.06</td>
<td>0.05</td>
<td>8.58 ± 0.04</td>
</tr>
<tr>
<td>4.07</td>
<td>0.1</td>
<td>7.73 ± 0.05</td>
</tr>
<tr>
<td>5.07</td>
<td>0.01</td>
<td>51.43 ± 6.84</td>
</tr>
<tr>
<td>5.14</td>
<td>1</td>
<td>58.74 ± 15.5</td>
</tr>
<tr>
<td>5.16</td>
<td>4</td>
<td>59.84 ± 19.5</td>
</tr>
</tbody>
</table>
### Effect of CO$_2$ on Sorption

<table>
<thead>
<tr>
<th>[CO$_2$], ppm</th>
<th>pH</th>
<th>Mass % Sorbed</th>
<th>$K_d$ (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric</td>
<td>9.27</td>
<td>21.0% ± 2.27%</td>
<td>2.48 ± 0.25</td>
</tr>
<tr>
<td>&lt; 1</td>
<td>9.30</td>
<td>36.7% ± 2.11%</td>
<td>5.48 ± 0.28</td>
</tr>
<tr>
<td>~1,000,000</td>
<td>9.28</td>
<td>~0%</td>
<td>N/A</td>
</tr>
<tr>
<td>Atmospheric</td>
<td>7.30</td>
<td>92.6% ± 0.97%</td>
<td>126.4 ± 0.28</td>
</tr>
<tr>
<td>~1,000,000</td>
<td>7.50</td>
<td>~0%</td>
<td>N/A</td>
</tr>
<tr>
<td>Atmospheric</td>
<td>4.85</td>
<td>75.3% ± 3.03%</td>
<td>39.3 ± 4.9</td>
</tr>
<tr>
<td>~1,000,000</td>
<td>4.75</td>
<td>28.78% ± 6.59%</td>
<td>4.43 ± 1.6</td>
</tr>
</tbody>
</table>
Kinetic Studies

- Two apparent partitioning phases
  - Rapid Initial Sorption
  - Slower “kinetic” phase
- Incomplete recovery during desorption
  - Approx. 10 µg U / g graphite remained sorbed
Sorption Isotherms

- Kinetic sorption and desorption data suggest at least 2 sites
- Fit w/ Freundlich Isotherm, $q = (0.930)c_{eq}^{0.37}$ (pH 5)
Kinetic Sorption Model

- **Two apparent partitioning phases**
  - Incomplete recovery during desorption
  - Approx. 10 µg U / g graphite remained sorbed

- **Kinetic Sorption Model Features:**
  - Sorption behavior has an equilibrium and kinetic fraction
  - Eq. fraction has higher $K_d$ than kinetic fraction
    - Can be sub-divided into a low/high solution mass region
  - Eq. fraction fills before kinetic fraction in partitioning
  - Kinetic fraction has first order rate constant of $\alpha = 0.01925 \text{ hr}^{-1}$
  - Equilibrium fraction maximum loading is 1.7 µg U / g graphite
Slow Flow Column Experiment

- 45-60 minute flow times used at constant concentration
- Tritium used as conservative tracer

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersion Coefficient</td>
<td>0.903 cm²/hr</td>
</tr>
<tr>
<td>Column Area</td>
<td>0.3845 cm²</td>
</tr>
<tr>
<td>Elution Rate</td>
<td>0.25 cm³/min</td>
</tr>
<tr>
<td>Column Length</td>
<td>9 cm</td>
</tr>
<tr>
<td>Graphite Mass</td>
<td>2.27 g</td>
</tr>
<tr>
<td>Graphite Bulk Density</td>
<td>1.794 g/cm³</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.365</td>
</tr>
</tbody>
</table>
Model Prediction vs. Experimental Results

![Graph showing model prediction vs. experimental results for different substances over time. The x-axis represents time in minutes, and the y-axis represents the concentration ratio C/C₀. The graph compares Uranium, Tritium, GoldSim Uranium, and GoldSim Tritium.]
Conclusions and Future Work

- Sorption to graphite is not insignificant
  - Particularly at near neutral pH
  - “Irreversibility” of sorption can provide additional barrier to release
- Carbonate complexation appears to suppress sorption

**Future Work**
- Sorption mechanism is still unknown
- Effects of graphite surface preparation needs to be examined
  - particularly surface oxidation
- Need longer term desorption data to bound desorption kinetics
- Data needed at elevated temperatures
- Isotherms need to be extended to lower concentrations
- Need to extend to other elements (Np, Pu, I, Tc)
Questions?